

## STUDIES OF CATALYTIC UPGRADING OF LOW-SEVERITY LIQUEFACTION PRODUCTS FROM LOW-RANK COALS

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### Introduction

The optimal liquefaction conditions for low-rank coals appear to be the use of a two stage process, where relatively low temperatures ( $380^{\circ}$ ) are used in the first stage because of the higher reactivity of low-rank coals and the tendency to coke at higher temperatures. This low-severity product can then be subjected to a secondary upgrading process to give a better fuel product. Much of the carboxylate groups of the coal are decarboxylated in the first stage, thus the second stage reaction involving catalytic hydrogenation does not waste much hydrogen on reactions with the evolved carbon dioxide. Transformations of the numerous oxygen functional groups of the low-rank coals occur during both the low-severity and the hydrotreating steps along with the depolymerization and other conversions, and the objective of our studies is to understand these transformations on a quantitative basis and correlate with the other liquefaction parameters, such as yields, changes in molecular weight distributions, and changes in hydroaromatic groups.

This paper is concerned with the catalytic hydrotreatment of a low-severity product obtained from the liquefaction of a Wyodak subbituminous coal in tetralin solvent at  $384^{\circ}\text{C}$  (1 hour) in carbon monoxide plus hydrogen sulfide. The low-severity product was separated into two fractions, a methylene chloride soluble fraction and methylene chloride insoluble fraction. The results from second stage liquefaction of the methylene chloride soluble fraction under various conditions will be reported here. This fraction comprised the major portion of the low-severity product. The second stage reaction used the same solvent as the first stage. This solvent was chosen because it does not contain oxygen and is a simple system whose products, naphthalene, decalin, methylindan, butyl benzene and dimers, can be easily distinguished in the reaction products. Two reaction temperatures ( $425^{\circ}\text{C}$  and  $450^{\circ}\text{C}$ ) were used in the high severity treatments. Runs for one or two hours were conducted. Hydrogen pressure was another variable during these investigations, although all reactions contained the same amount of the sulfided Co-Moly catalyst.

## Experimental

In a typical run, methylene chloride solubles (20 g including tetralin solvent) obtained from the low-severity Wyodak liquefaction in tetralin and 0.80 g of sulfided Co-Moly catalyst (AMOCAT) were sealed in a 75 ml tubing bomb. The tubing bomb was evacuated and pressurized with 300 or 400 psi of hydrogen, if needed in the test. The tubing bomb was lowered into a fluidized bed sand bath maintained at the desired temperature (425° or 450°C). The bomb was heated with constant agitation for the desired time (1 or 2 hrs). At the end of the reaction, the tubing bomb was removed from the sand bath, cooled to room temperature and slowly depressurized. The raw product slurry obtained on opening the tubing bomb was transferred to a beaker with methylene chloride and was separated into various product fractions.

The following products were obtained from the product work-ups of the high severity liquefaction product slurry (1):

- 1) methylene chloride insolubles
- 2) pentane insolubles
- 3) low-boiling (less than 160°C/1.4 torr) distillate (mainly solvent, see below)
- 4) high boiling (160-240°C/1.4 torr) distillate (contains some solvent and dimers, see below)
- 5) vacuum bottoms (nondistillable material)

The conversion was calculated as the conversion of the pentane insoluble fraction of the low-severity material to pentane soluble material during the high severity liquefaction, and these data are given in Table 1. Of course this conversion is not the only description of reaction progression of interest. The product yield (coal-derived material) in the distillates is also very important. Also of interest is the retrograde reaction which results in methylene chloride insoluble material.

The product distillate yields were then calculated by subtraction of the solvent (tetralin, naphthalene, and decalin) from the low-boiling distillate yield and adding this to the result obtained by subtraction of the solvent-derived dimers (bitetralin, binaphthyl, naphthyltetralin, etc.) from the high boiling distillate yield. The solvent distillate yields are a combination of the amounts of tetralin, naphthalene, decalin in both distillates plus the solvent-derived dimers in the high boiling distillate.

The volatile products were characterized by GC-FID and GC/FTIR/MS, the nonvolatile products were characterized by photoacoustic FTIR, solid state or solution <sup>13</sup>C NMR and weight average molecular weight determinations (low angle laser light scattering photometry).

## Results and Discussion

### Conversions

The data summarized in Table 1 reveal that the degree of conversion is dependent on several factors. The reaction at 425°C for one hour with no hydrogen present gave a conversion of only 30%. Raising the processing temperature to 450° for the same time and with no hydrogen pressure increased the conversion to 84%. Also increasing the contact time from one hour at 425° to two hours (no hydrogen) increased the conversion to 78%. In the tests with 400 psi of hydrogen, the conversions increased to 66% at 425°C for one hour and to 92% at 450° for one hour. The two hour reaction under hydrogen (charged to 300 psi, run one hour, recharge to 300 psi, run another hour) gave 80% conversion. Thus the conversion is directly proportional to the reaction

temperature, the reaction time, and the added hydrogen pressure.

Another interesting feature of the high severity reactions was the solvent conversion, that is tetralin to naphthalene as a result of hydrogen donation to the coal-derived material. The tetralin to naphthalene ratios in the products from high severity treatments were calculated from the GC/FID determinations of the volatile material (low boiling distillate plus a very small amount in the high boiling distillate) and compared with the ratio initially present in the low-severity product. These ratios are also reported in Table 2. The initial tetralin/naphthalene ratio in the low-severity product was 27, indicating the relatively low hydrogen consumption in the low-severity reaction.

The high severity reactions changed the tetralin/naphthalene ratios significantly. The reaction at 425° for one hour without added hydrogen gave a ratio of 3.31. This corresponds to the formation of 3.7 g of naphthalene (24 mmoles) or transfer of 48 mmoles of H<sub>2</sub> from the tetralin to the coal material during the reaction. Increased reaction time further decreased the ratio (to 2.76). Raising the temperature to 450° for one hour, with no hydrogen added, dropped the ratio even more to 2.06, which indicates that more hydrogen is transferred to the coal fragments at higher temperatures and is consistent with the more extensive conversion which was observed at the higher temperature. When molecular hydrogen was added to the reaction mixture (425°, one hour, 400 psi H<sub>2</sub>), the ratio of tetralin to naphthalene was somewhat greater (4.16) than that observed when no hydrogen was added (3.31). Longer reaction times with hydrogen present similarly gave higher ratios (2.51) than those reactions with no hydrogen present (2.76), but lower ratios than the one hour reactions. Thus the tetralin/naphthalene ratios for the high-severity ratios are inversely proportional to the reaction temperature and the reaction time and directly proportional to the hydrogen present. These results are in agreement with the conversion percentages, that is the higher the conversion, the more hydrogen was transferred.

#### Methylene chloride insoluble product

The methylene chloride insoluble material isolated from the reaction products consisted of the added Co-Moly catalyst plus only about 1% of material derived from the starting low-severity material. The insoluble material was studied using photoacoustic FTIR spectroscopy and was found to contain both alkyl and aromatic groups. This material may be the product of retrograde or cross-linking reactions of some of the macromolecules of the low-severity product which occurred during the catalytic high severity reaction. Although it cannot be described exactly as coke, since it has alkyl groups, the retrograde reaction which produces these small amounts may be similar to that described as "coking."

Since the amount of this material is insignificant even in reactions at 450°C with no hydrogen pressure, the soluble low-severity product is not likely to be the source of the coked material obtained during some liquefaction experiments with whole coals. More likely the source is the more aromatic and less soluble part of the coal which continues to donate hydrogens to the more soluble portions until it becomes the coke.

#### Pentane insoluble product (Methylene chloride soluble)

The decrease in the amount of the pentane insoluble fraction in going from the low-severity material to the high severity product has been discussed above in terms of the conversion of the reaction, which was shown to be highly dependent on the conditions chosen for the high severity reaction. The

question of interest here is how did the structure and properties of the recovered pentane insoluble fraction change in comparison with the pentane insoluble fraction of the starting low-severity material, as a result of the high severity liquefaction carried out under different conditions

The changes in the molecular weights of the coal macromolecules during second stage processing of this methylene chloride soluble fraction from low-severity liquefaction of Wyodak was investigated by static low angle laser light scattering (LALLS) photometry in tetrahydrofuran solvent. This product was nondistillable and nonvolatile. Rayleigh scattering factors were measured for the dilute THF solutions of the pentane insoluble products and corrected by means of the Cabannes factors which were determined for each of the solutions used. The corrected Rayleigh factors gave a linear reciprocal scattering plot ( $KC/R_{90}$  versus  $C$ ) with an  $r^2$  of 0.99. The weight average molecular weight of the pentane insoluble fraction of the starting low-severity material was  $5.6 \times 10^5$  daltons. The weight average molecular weight of the pentane insoluble material recovered from the high severity treatment in tetralin solvent at  $425^\circ\text{C}$  for one hour in the absence of added hydrogen was  $6.27 \times 10^5$  daltons, a significant increase over that observed for the pentane insoluble fraction of the starting Wyodak low-severity product. An increase in molecular weight was also observed for the pentane insoluble fractions recovered from the high severity treatment of Big Brown lignite in work done earlier (2). There may be two reasons for the increase. First, a selective reaction of the lower molecular weight material during the heating at  $425^\circ\text{C}$  would have changed the distribution to a higher molecular weight. Second, the liquefaction reactions may involve some retrograde or polymerization reactions which would increase the molecular weight distribution of this fraction.

The pentane insoluble material recovered from the high severity reaction at  $425^\circ$  for one hour with hydrogen (400 psi) gave a weight average molecular weight of  $4.06 \times 10^6$ . Again this value is larger than that of the starting pentane insoluble material, indicating either the change in distribution by preferential reaction of lower molecular weight material or retrograde reactions were occurring. The main difference between this material and that isolated from the high severity reaction carried out without hydrogen is that the amount of pentane insoluble material obtained in the presence of hydrogen is much smaller, possibly as a result of minimization of the retrograde reaction by the molecular hydrogen.

Further characterization of the pentane insoluble fractions were carried out using photoacoustic-FTIR and solid state  $^{13}\text{C}$  NMR spectroscopy. FTIR spectra of the fractions recovered from the high severity reactions when compared with that of the low-severity fraction showed an increase in the aromatic absorptions at  $1600\text{ cm}^{-1}$ . The carbonyl absorptions in these products were insignificant. The increase in aromatics was confirmed by the NMR spectra. The low-severity material showed an aromatic carbon to aliphatic carbon ration of 1.47. This ratio was 3.25 in the pentane insoluble fraction from the reaction at  $425^\circ$  for one hour in tetralin in the presence of 400 psi of hydrogen. The ratio was even higher in the product of the reaction at  $425^\circ$  for 2 hours in the absence of hydrogen (3.84). These NMR data for the various fractions show that there is a preferential solubilization of the aliphatic material. Two explanations are possible. First, aliphatic material may be cleaved from the aromatic clusters of the coal macromolecules. Second, the more aliphatic members of the distribution of macromolecules may be preferentially degraded during the high-severity liquefaction. The higher ratio for the reaction in the absence of hydrogen as compared with that for the reaction in the presence of hydrogen may be explained in several ways.

First, aromatics may be converted to hydroaromatics in the presence of hydrogen. Second, alkyl radicals formed in the thermal degradations may be converted to alkanes by trapping with molecular hydrogen when present or by reacting with coal structures which result in formation of aromatics in the absence of hydrogen.

#### Solvent-derived distillate

The low boiling distillates obtained from low-severity treatment of Wyodak in tetralin and the high-severity treatments under various conditions were characterized using GC/MS. The low-severity low boiling distillate consisted mainly of tetralin and naphthalene (T/N ratio = 27) along with small amounts of decalin and methylindan. No significant amounts of solvent-related dimers were found in the low-boiling distillates. The coal derived material in this distillate is discussed separately below.

The high boiling distillate (160-240°C/1.4 torr) consisted of small amounts of tetralin and naphthalene and the dimers (bitetralyl, binaphthyl, naphthyltetralin, naphthyldecalin, etc.) derived from the solvent in addition to the coal-derived material. Some of these dimers were present in the distillate from the methylene chloride soluble fraction of the low-severity material. The amounts of this material formed from the solvent was greatest at the lower (425°C) temperatures when no hydrogen was present and was the least at the high temperatures with or without hydrogen pressure.

#### Product distillate

A small fraction of the low boiling distillate consisted of coal derived material such as phenols, alkanes and arylalkanes. The volatile material in the high boiling distillate fraction which was derived from the low-severity product was mainly n-alkanes plus the usual variety of 1 to 4-ring aromatics (unsubstituted and alkyl substituted). Substantial amounts of diphenyl ethers and dibenzofuran were found.

The coal-derived product was only 1% of the amount of the low boiling distillate of the methylene chloride soluble fraction of low-severity material but was 2/3 of the high boiling distillate of the low-severity material. The sum amounted to 33% of the mass of the methylene chloride soluble low severity material. As a result of the high severity treatments, the amount of distillable product increased in all cases; the highest yield was obtained for the 450°C reaction with hydrogen, where 81% of the total liquefaction product was the distillate.

#### Vacuum bottoms

The vacuum bottoms are the undistillable materials left after distillation of the pentane solubles at 1.4 torr. The amounts of the vacuum bottoms obtained from the low-severity product of Wyodak was 0.56 g/batch or 15.6% of the total coal-derived material in the low-severity product. The amounts of vacuum bottoms increased slightly for the high-severity treatment at 425°C with or without added hydrogen. However, raising the reaction temperature to 450°C resulted in decreased amounts of vacuum bottoms.

The vacuum bottoms were characterized using infrared spectroscopy, molecular weight determinations, and proton-decoupled solution <sup>13</sup>C NMR in deuterated chloroform. Both the infrared spectra and the solution NMR spectra indicate that the vacuum bottoms obtained from the high severity liquefactions are more aromatic than the distillates, but not nearly as aromatic as the pentane insoluble fractions discussed above. The bottoms obtained from the reaction at 450°C with no hydrogen added had an aromatic carbon to aliphatic

carbon ratio of 1.73.

The vacuum bottoms fractions contained some material which sublimed at 0.25 torr and 250°, but the remainder exhibited large Cabannes factors and large Rayleigh scattering, giving molecular weights of 10<sup>5</sup> daltons.

#### Conclusions

The low severity methylene chloride soluble product consists of a high molecular weight pentane insoluble fraction, a high molecular weight vacuum bottoms fraction and one third distillable oils. This material was converted by the high severity conditions into a product consisting of small amounts of a higher molecular weight pentane insoluble fraction, a high molecular weight vacuum bottoms fraction, and an increased amount of a distillable oil product. The relatively small amount of the high molecular weight aromatics in the distillate or volatiles may be a consequence of the absence of very large polycondensed aromatic clusters in the low severity product. When the macromolecules are cleaved they go all the way to small molecular weight species. A similar distribution was observed in the Wyodak ITSL product reported by Moroni (3).

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#### References

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TABLE 1

#	Reaction Conditions	PI	Products (in gms)		Conversion (%) (PI → PS)	T/N Ratio
			Prod. Dist.* (%)**	B		
1.	Starting Material (L,S)	1.60	1.05 (33.0)	0.56	--	27.0
2.	425-1-OH <sub>2</sub>	1.10	1.27 (43.0)	0.57	30.00	3.26
3.	425-2-OH <sub>2</sub>	0.33	1.76 (63.0)	0.73	78.7	2.76
4.	425-1-400H <sub>2</sub>	0.52	1.27 (50.8)	0.71	66.40	4.16
5.	425-1+1-300+300	0.31	1.66 (62.64)	0.68	80.1	2.51
6.	450-1-OH <sub>2</sub>	0.24	1.67 (69.87)	0.48	84.50	2.06
7.	450-1-400H <sub>2</sub>	0.15	2.23 (81.10)	0.37	92.0	3.40

\* Wt %: does not include low boiling phenolic products (<60°C at 1.4 torr)

\*\* % of total coal-derived products.

PI = Pentane Insolubles

PS = Pentane Solubles

B = Vacuum Bottoms

T/N = Tetralin/Naphthalene

L,S = Low Severity